Project 1019085

Influence of Reactive Transport on the Reduction of U(VI) in the Presence of Fe(III) and Nitrate: Implications for U(VI) Immobilization by Bioremediation/Bioba

Wood, Brian D.
Oregon State University

RESULTS TO DATE: The research in Y02 was focused on the design and execution of experiments in the abiotic reduction of U(VI) by simulated biogenic Fe(II) in porous medium under conditions of flow, and on the development of appropriate descriptive theory. Because the project started only in February of this year, we are reporting some work in progress. Major accomplishments and studies currently underway are listed below.

1. Flow System for Study of U(VI) Reduction by Fe(II):A batch, fully mixed, open-flow system has been designed and constructed to maintain strictly anaerobic conditions, and automatically collect samples at specified intervals. This system consists of several inlet bottles (using He sparging), an HPLC pump, stir cell, inline pH and electrical conductivity (and data logging computer), and an anaerobic sampling system (controlled by a second computer). The system has been extensively tested using tracers and reactive chemicals and allows to perform experiments in stir-batch or short column mode. Both characterization of sorption reactions and abiotic reduction of U(VI) by Fe(II) has been and will be investigated using the system.

2. Characterization of Model Sediment Materials. Goethite-coated sand was used at initial stage of the project as a model sediment to study the abiotic reduction of U(VI) by Fe(II). It was chosen because the relative complexity of its surface property compared with pure iron oxide is more close to field condition, yet its relative simplicity compared with field sediment could allow better understanding of experimental results at mechanistic scale. The model sediment has been synthesized and its surface properties were quantified.

3. Sorption Isotherms of Fe(II) and U(VI): The process of U(VI) reduction by Fe(II) was found to proceed only on sediment surface. In order to quantify the surface behavior of Fe(II) and U(VI), a series of flow experiments have been conducted in a batch-stir system to determine the Fe2+ adsorption isotherm on the model sand. The sorption results indicated that Fe(II) sorption/desorption was generally a kinetic process driven by the thermodynamic equilibrium pressure. The finding has an important implication for a field system with groundwater flow, i.e., Fe(II) sorption will be influenced not only by traditional factors, like surface complexation constants, site density, etc, but also by the flow rate which controls the contact time of Fe(II) with sediment surface. A better model of describing Fe(II) sorption will therefore have to consider both equilibrium and kinetic factors. Experiments of the U(VI) sorption isotherm is currently underway.

4. Kinetic Rate of U(VI) Sorption and Reduction by Fe(II) with/without CO2: Flow experiments are planned to determine the U(VI) reduction rate at different Fe2+ surface coverage and differing carbonate concentration using the designed flow system in both stir-batch and column modes. Two important hypotheses will be tested in these planned experiments. The first hypothesis is that U(VI) reduction by Fe(II) is through an electron transfer process when both U(VI) and Fe(II) are sorbed or U(VI) is reduced by sorbed Fe(II) but U(VI) itself could be in aqueous phase. Our theoretical modeling indicated that if electron transfer requires both U(VI) and Fe(II) sorption on surface, the overall U(VI) reduction rate will exhibit parabolic shape with increasing Fe(II) loading on the surface. On the other hand, a linear kinetic rate with increasing Fe(II) loading will be expected if electrons directly transfer from sorbed Fe(II) to aqueous U(VI). This study will not only elucidate which process controls electron transfer, a fundamental mechanism of U(VI) reduction by Fe(II), but also provide a rate expression at mechanistic level that will better predict the kinetics. The second hypothesis is how the concentration of CO2 influences the kinetic rate of U(VI) reduction by Fe(II). Carbonates can form complexes with U(VI) at circumneutral pH and

increase U(VI) mobility. Carbonates may also form complexes with Fe(II) and may decrease the solubility and sorption of Fe(II) by forming precipitated Fe(II) phase, for example, siderite. A set of experiments are planned to answer whether the Fe(II) reactivity will be decreased by forming Fe(II) solid phase, or whether Fe(II) in solid phase could still pass electron to U(VI) even in aqueous phase as U(VI)-complex species.

Currently, we have completed one set of experiments characterizing the kinetic sorption of U(VI) in Hanford sediments under conditions of flow with varying carbonate concentrations (concentration of 0, 5, 10, and 20 mg/L as CO3. A dramatic effect of carbonate concentration can be observed. At the highest carbonate concentrations, the U(VI) is almost entirely complexed, and the Uranium moves as essentially a conservative tracer. At zero carbonate concentration, however, significant kinetic sorption effects can be observed, and the resulting U(VI) breakthrough curves are correspondingly asymmetric. Parallel experiments for FRC sediments are currently underway.

5. Biofilm Formation measurements. In Task 2 of the proposed work, a set of experiments are described in which confocal microscopy was to be used to examine biofilm formation in 2-dimensional systems; this work was designed to help assess how important mass transfer resistance through biofilms might be in the process of metal reduction. Recently, new nuclear magnetic resonance (NMR) instruments have become available at the Environmental Molecular Sciences Laboratory (EMSL) that can, in principle, accomplish the same result but in a more-physically-relevant 3-dimensional format. Several blocks of user time have been requested (by B. Wood), supported at no cost to the project as part of the EMSL?s user facility mission. We have now conducted several exploratory investigations of the use of NMR for non-destructive measurement of growing biofilms of Shewanella putrefaciens MR-1 in porous media. The most recent efforts have focused on using fluid flow through the porous medium to filter the NMR data in such a way as to provide an improved signal. This effort has lead to positive results, and allowed the dynamic measurement of biomass in the porous material at unprecedented resolutions. These initial efforts were somewhat limited in scope due to the time constraints imposed by the need to develop a new method; however, additional NMR time is being requested, and we intend to further develop the method to provide truly 3-dimensional measurements of biofilm distribution within the porous matrix at an expected resolution of 30 microns. If successful, these experiments will be extended to examination of Shewanella putrefaciens MR-1 under uranium-reducing conditions. Two publications are currently in progress for this work.